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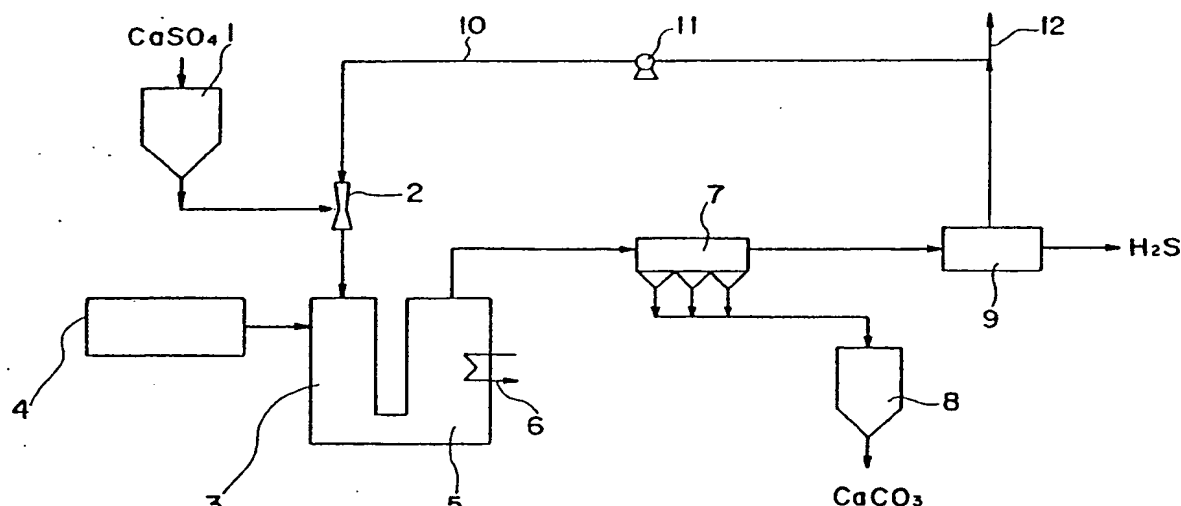
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(54) Exhaust gas desulphurisation and treatment of  $\text{CaSO}_4$  solids produced therein

(57) A method of treating solids containing the calcium salt of a sulfuric oxyacid comprising feeding to a reduction reactor (3) a reducing gas stream (4) containing hydrogen and/or carbon monoxide and having a first predetermined temperature and dry particles containing the calcium salt of sulfuric oxyacid (1) and having a predetermined mean particle size to reduce the calcium salt to calcium sulfide, subsequently cooling the gas stream obtained from the reduction reactor to a second temperature in a carbonation reactor (5) to react the calcium sulfide with carbon dioxide and water vapor and produce calcium carbonate and hydrogen sulfide, guiding the resulting gas stream from the carbonation reactor into a dust collecting unit (7) to collect solid particles, and further collecting the hydrogen sulfide (9) from the gas stream flowing out from the dust collecting unit.

Fig. 1



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Fig. 1

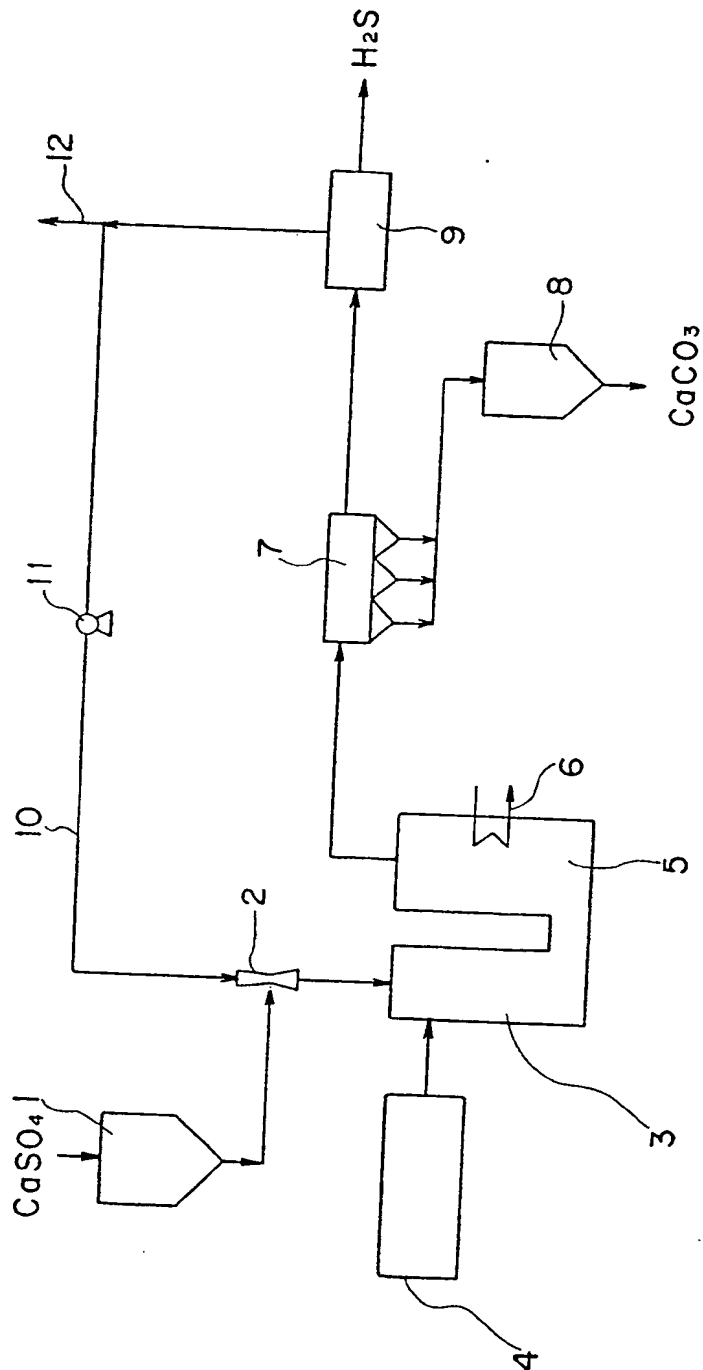
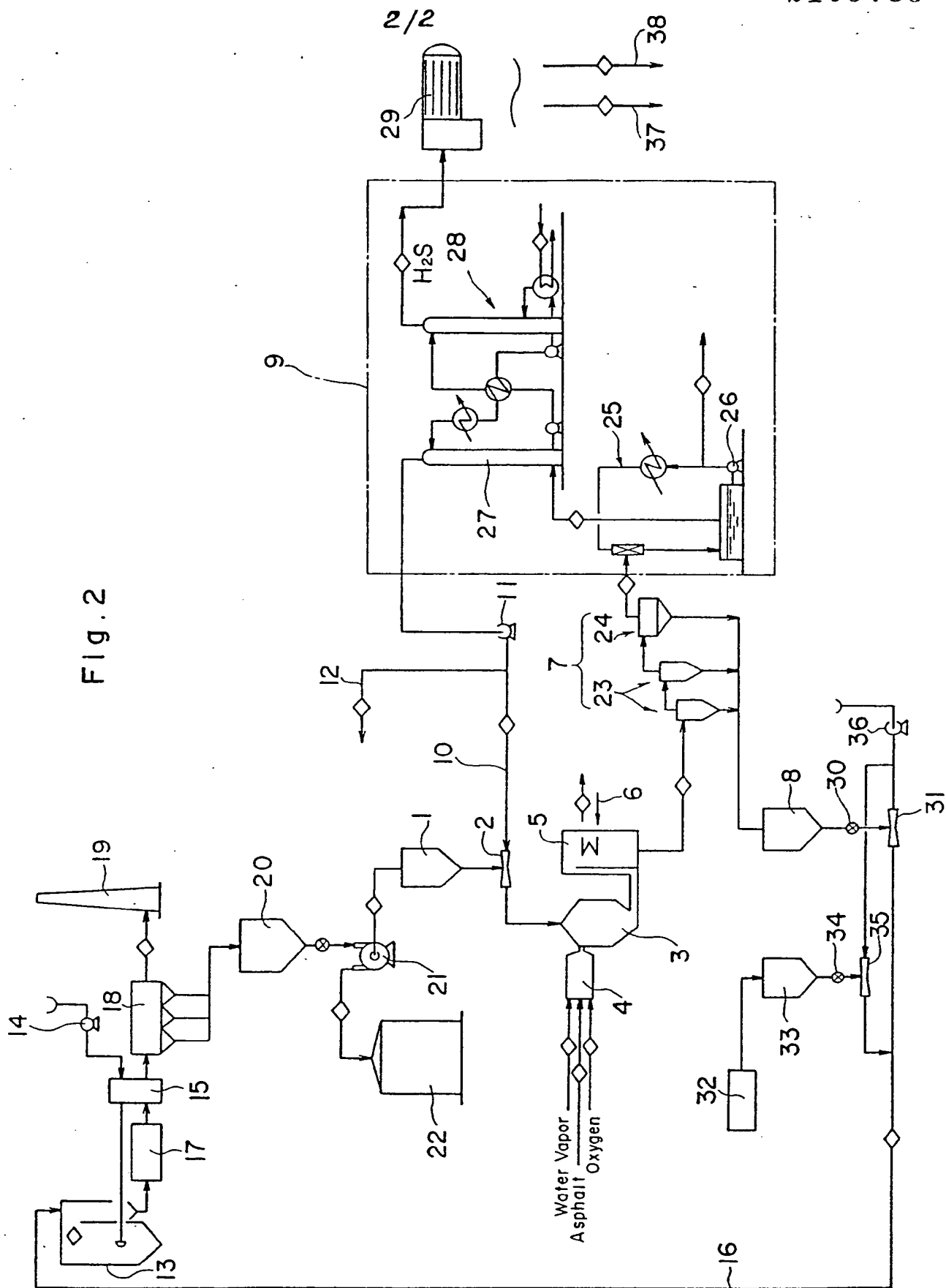


Fig. 2



## SPECIFICATION

**Treatment of solids containing calcium salt of sulfuric oxyacid and method of purifying exhaust gas utilizing same**

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The present invention relates to a dry method of treating solids containing the calcium salt of a sulfuric oxyacid such as gypsum, and to a process utilizing the method for purifying exhaust gases from boilers or furnaces such as incinerators by efficiently removing harmful acid substances from the gas.

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A dry method is already proposed of purifying the exhaust gas from a boiler or waste incinerator or like furnace by dispersing particles of a Ca-type absorbent (quick lime, slaked lime, limestone, dolomite or the like) directly into the furnace or flue to cause the absorbent particles to absorb harmful acid substances, such as sulfur oxides ( $\text{SO}_x$ ), from the gas for removal. With this method, the absorbent particles are partly converted to gypsum ( $\text{CaSO}_4$ ) by the reaction with the sulfur oxides and collected by a dust collector along with other solid particles as soot and dust. The soot and dust obtained, although containing gypsum, further contain fly ash and unreacted absorbent components and therefore are not usable for preparing gypsum board or cement for which gypsum is generally used. Further if the furnace is large-sized, the soot and dust, which are produced in large quantities, can not be discarded directly, since various problems will then result. Further if the gypsum obtained has a relatively high purity and is useful, problems will be encountered in treating the gypsum in the event of excess supply.

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Accordingly, methods have been proposed which include one comprising calcining gypsum in a kiln in the presence of an insufficient amount of air to obtain a quick lime and a gas containing  $\text{SO}_2$  and recording sulfuric acid from the  $\text{SO}_2$ , and a method comprising converting gypsum to calcium sulfide in a reducing atmosphere in a kiln with a limited supply of air, preparing an aqueous slurry from the resulting calcium sulfide after pulverization and passing carbon dioxide through the slurry to collect hydrogen sulfide.

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However, the conventional methods not only require a large-sized apparatus but also involve uneven heating by the kiln to render the resulting quick lime or calcium sulfide less reactive owing to accelerated crystallization and cause trouble to the subsequent treatment. Moreover, the methods are unsatisfactory from the viewpoint of savings in energy.

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An object of the present invention is to overcome the foregoing problems heretofore encountered.

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According to a first aspect of the invention, there is provided a method of treating solids containing the calcium salt of a sulfuric oxyacid comprising feeding to a reduction reactor a reducing gas stream containing hydrogen and/or carbon monoxide and having a first predetermined temperature and dry particles containing the calcium salt of sulfuric oxyacid and having a predetermined mean particle size to reduce the calcium salt to calcium sulfide, subsequently cooling the gas stream obtained from the reduction reactor to a second temperature in a carbonation reactor to react the calcium sulfide with carbon dioxide and water vapor and produce calcium gas stream from the carbonation reactor into a dust collecting unit to collect solid particles, and further collecting the hydrogen sulfide from the gas stream flowing out from the dust collecting unit.

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The above method is not limited only to the treatment of gypsum resulting from the purification of exhaust gases but is useful also for solids containing the calcium salt of any sulfuric oxyacid capable of giving calcium sulfide upon reduction.

Examples of sulfuric salts of sulfuric oxyacids are, in addition to gypsum (calcium sulfate), calcium sulfite ( $\text{CaSO}_3$ ), calcium thiosulfate ( $\text{CaS}_2\text{O}_3$ ) and calcium polythionate ( $\text{CaS}_x\text{O}_6$ ).

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According to a second aspect of the invention, there is provided a method of purifying an exhaust gas containing sulfur oxides by spraying dry particles of a Ca-type absorbent having a predetermined mean particle size into the exhaust gas to cause the absorbent to absorb the sulfur oxides and thereafter collecting by a dust collecting unit the absorbent particles along with other particles contained in the exhaust gas, the method being characterized by feeding to a reduction reactor the used absorbent particles collected by the dust collecting unit and a reducing gas stream containing hydrogen and/or carbon monoxide and having a first predetermined temperature to reduce calcium sulfate contained in the used absorbent particles to calcium sulfide, subsequently cooling the gas stream obtained from the reduction reactor to a second temperature in a carbonation reactor to react the calcium sulfide with carbon dioxide and water vapor and produce calcium carbonate and hydrogen sulfide, guiding the resulting gas stream from the carbonation reactor into a second dust collecting unit to collect solid particles, and spraying the solid particles again into the exhaust gas as regenerated absorbent particles.

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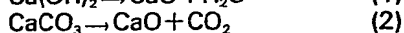
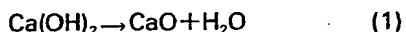
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The Ca-type absorbents to be used in the present method include limestone ( $\text{CaCO}_3$ ), slaked lime [ $\text{Ca}(\text{OH})_2$ ], quick lime ( $\text{CaO}$ ), dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), slaked dolomite [ $\text{Ca}(\text{OH})_2 \cdot \text{Mg}(\text{OH})_2$  or  $\text{Ca}(\text{OH})_2 \cdot \text{MgO}$ ], calcined dolomite ( $\text{CaO} \cdot \text{MgO}$  or  $\text{CaCO}_3 \cdot \text{MgO}$ ) and any material containing  $\text{CaO}$  or capable of forming  $\text{CaO}$  at a high temperature. Accordingly, the particulate Ca-type absorbent

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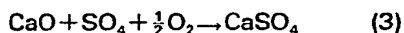
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originally contains CaO or produces CaO through the following reactions at a high temperature.



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CaO absorbs sulfur oxides ( $\text{SO}_x$ ) from the exhaust gas upon reacting therewith as represented by the following equations.



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The  $\text{CaSO}_4$  shells formed on the surfaces of absorbent particles by the reactions (3) and (4) have a compact texture and inhibit harmful acid substances such as  $\text{SO}_x$  from diffusing into the particles, consequently reducing the reactivity of the absorbent. However, the  $\text{CaSO}_4$  shells are converted to calcium carbonate ( $\text{CaCO}_3$ ) by the treatment according to the first aspect described, whereby the particulate absorbent is regenerated. The regenerated absorbent, if sprayed into the exhaust gas again, greatly reduces the amount of fresh absorbent to be supplied.

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Of the Ca-type absorbents mentioned above, dolomite, slaked dolomite and calcined dolomite have a large void volume, permit harmful acid substances to readily diffuse into the particles thereof and are therefore advantageous. Since the extraneous components such as  $\text{MgO}$  do not participate directly in the regeneration reactions, the change of such components will not be described for the sake of simplified description.

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Exhaust gases, especially those from coal boilers and waste incinerators generally contain fly ash of large particle sizes in addition to harmful acid substances. In such a case, it is desirable to classify the particles collected by the first dust collecting unit into a coarse particle portion primarily containing fly ash and a fine particle portion primarily containing absorbent particles not larger than a predetermined particle size and thereafter regenerate the fine particle portion only. In the case of fuel oil boilers, the amount of fly ash is lesser than that of absorbent particles, so that the classification step is not always required.

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Various features and advantages of the present invention will be readily understood from the embodiments to be described below with reference to the accompanying drawings.

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Figure 1 is a flow chart showing a system for treating solids containing the calcium salt of sulfuric oxyacid according to the invention; and

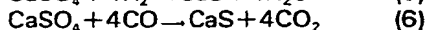
Figure 2 is a flow chart showing a system for purifying exhaust gases according to the invention.

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Indicated at 1 in Fig. 1 is a hopper containing fine particles of used Ca-type absorbent (partly containing gypsum) or solids containing the calcium salt of a sulfuric oxyacid, such as high-purity gypsum. The fine particulate material is sprayed from the hopper 1 into a reduction reactor 3 as entrained in a carrier gas by an ejector 2 which is an example of a dispersing nozzle. Connected to the reduction reactor 3 is a reducing gas generator 4, in which a hydrocarbon, such as asphalt, is partially burned with oxygen and water vapor to produce a reducing gas having a high temperature and containing carbon monoxide and hydrogen. Within the reduction reactor 3, therefore, the  $\text{CaSO}_4$  component of the particulate material is reduced to calcium sulfide ( $\text{CaS}$ ) according to the following equation.

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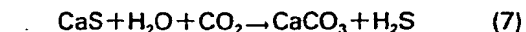
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Provided downstream of the reactor 3 is a carbonation reactor 5 equipped with a cooler 6 (which may be a heat exchanger or a device adapted to evaporate water on spraying). The gas stream from the reduction reactor 3 is cooled in the carbonation reactor 5, whereby the  $\text{CaS}$  is carbonated and further gives hydrogen sulfide according to the following equation.

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The gas stream flowing out from the reactor 5 and containing fine carbonated particles and  $\text{H}_2\text{S}$  is then subjected to solid-gas separation by a dust collecting unit 7, and a fine solid particulate portion consisting primarily of fine carbonated particles is collected by a calcium carbonate hopper 8.

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The gas stream from the dust collecting unit 7 is sent to a hydrogen sulfide collector 9, by which the  $\text{H}_2\text{S}$  is collected. The collected  $\text{H}_2\text{S}$  may be converted to elemental sulfur by the Claus process or to sulfuric acid by a wet process, or may be used as a material for chemical synthesis.

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The gas stream separated from the  $\text{H}_2\text{S}$  contains hydrogen, carbon monoxide and carbon dioxide as unreacted components, so that it is advantageous to recycle the gas stream through

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a feedback line 10 equipped with a compressor 11 as a carrier gas for feeding fine particles from the hopper 1 to the reduction reactor 3. The carrier gas, when containing impurities (mainly nitrogen) at an excessively high concentration, requires use of reactors 3, 5 of increased capacity and adversely affects the formation of calcium carbonate. Accordingly the carrier gas is partially purged suitably via a purge line 12.

The smaller the fine particles passing through the reactors 3, 5, the better is the result, because the reduction of the particle size assures smooth diffusion of heat and the reactants into the particles, consequently shortening the reaction time required and permitting use of reactors 3, 5 of reduced size. Further because of an improved heat transfer efficiency then achieved, the reduction reactor 3 assures uniform heating to inhibit crystallization of CaS, while smooth carbonation takes place in the reactor 5, giving highly reactive calcium carbonate. In view of the power consumption needed for pulverization, the fine particulate material to be used for practicing the present invention is up to 10 microns, preferably 1 to 3 microns, in mean particle size.

The ejector 2 serving as a dispersing nozzle and cooperating with the carrier gas pressure-fed through the feedback line 10 acts to uniformly disperse the pre-pulverized particulate material from the hopper 1 into the reducing gas within the reactor 3, whereby the  $\text{CaSO}_4$  component can be reduced with a high reactivity. In place of the fine particulate material which has been finely divided, solids containing the calcium salt of sulfuric oxyacid may be pulverized on site by a jet mill or the like before being fed to the dispersing nozzle 2.

Usually, the  $\text{CaSO}_4$  component contains crystal water and loses the water at a high temperature of 100 to 200°C. If this dehydration reaction occurs at the portion of the dispersing nozzle 2 which is exposed to a high temperature, it is likely that the nozzle 2 will become plugged up or particles will agglomerate (to result in a reduced reactivity), leading to poor economy. Accordingly, it is desirable to calcine the particulate material to render the  $\text{CaSO}_4$  anhydrous before the material reaches the nozzle 2.

For the regeneration of the  $\text{CaSO}_4$  component to  $\text{CaCO}_3$ , it is advantageous that the reducing gas concentration within the reactor 3, and the water vapor concentration and the carbon dioxide concentration within the reactor 5 be maintained at a high level. For this purpose, concentrated oxygen, especially concentrated oxygen having a concentration of at least 95%, is more preferable than air which contains large amounts of nitrogen and other impurities, as the oxygen source to be used for partially burning a hydrocarbon within the reducing gas generator 4.

The reduction reactions of Equations (5) and (6) take place at a temperature of not lower than 700°C. While these reactions progressively proceed from the surface of the particles inward, the reaction velocity is dependent on the rate of diffusion of  $\text{H}_2$  or CO from the surface of the particle into the interior, so that the reaction is accelerated with decreasing particle size. Because the rate of diffusion is the predominant factor, the rise of the reaction temperature to more than 900°C is not very effective for the reduction of  $\text{CaSO}_4$  to CaS. Further temperatures over 1100°C promote crystallization of the CaS produced, inhibiting the diffusion of  $\text{H}_2$  or CO into the particles and adversely affecting the subsequent carbonation, hence objectionable. Accordingly, it is advantageous that the temperature within the reduction reactor 3 be adjusted to 700 to 900°C.

The carbonation reaction of Equation (7) is an equilibrium reaction, and it is required to maintain the temperature at a level of up to 500°C for the completion of the reaction, while it is known that this carbonation reaction proceeds at a low velocity. It is therefore necessary to maintain the reaction temperature at the highest possible level within the range of up to 500°C for the promotion of the reaction. Although it was not clear whether the carbonation reaction can be carried out within a practically useful period of reaction (particle retention) time, we have found that the desired reactivity can be achieved with a reaction time of about 3 to 20 seconds by using particles of reduced mean particle size (especially 1 to 3 microns) at a reaction temperature of 300 to 500°C.

Next, experiments will be described which were conducted to substantiate the advantages of the foregoing method of treatment.

## 55 EXPERIMENT I

Hollow cylindrical refractory bricks, 20 cm in inside diameter, were stacked up to a height of 12 m to build an experimental reaction column corresponding to the reactors 3 and 5 of Fig. 1 combined together. A combustion chamber (corresponding to the reducing gas generator 4) made of refractory bricks was provided on the top of the column. A dispersing nozzle (corresponding to the ejector 2) was installed at the column top under the chamber. A water spray nozzle (corresponding to the cooler 6) was attached to the column at a position 1.5 m below the nozzle. Temperature measuring thermocouples were inserted into the reaction column at a position 0.5 m below the nozzle and at a position 6 m below the water spray nozzle. The portion of the reaction column above the water spray nozzle was externally covered with an electric heater, which was protected with heat insulating bricks and iron pipe from outside. The

resulting assembly was further covered with a heat insulator. The other portion of the column was protected only with an iron pipe. The water spray nozzle used was one called a supersonic nozzle which is capable of producing atomized water (fine water droplets). The outlet of the reaction column was provided with a Jetclone Collector (high-performance cyclone, product of Nippon Pneumatic MFG. Co., Ltd.) for trapping dust.

- 5 Town gas was burned in the combustion chamber to heat the reaction column to a specified temperature. An experiment was then conducted for 2 hours under the following conditions. First, the town gas was replaced by carbon monoxide and hydrogen. Carbon monoxide was fed to the chamber at a flow rate of 14 Nm<sup>3</sup>/h (N representing standard state), hydrogen at 6 Nm<sup>3</sup>/h, and air at 34.8 Nm<sup>3</sup>/h for partial combustion (to maintain a predetermined reaction temperature). On the other hand, anhydrous gypsum (purity 99%) finely divided to a mean particle size of 3 microns and serving as a solid containing the calcium salt of a sulfuric oxyacid was fed at a rate of 13.6 kg/h to the dispersing nozzle at the column top, as entrained in a carrier gas composed of 50% of carbon monoxide and 50% of hydrogen and supplied at a rate of 24.2 Nm<sup>3</sup>/h, whereby the finely divided gypsum was dispersed into the hot combustion gas from the combustion chamber, the carrier gas being accelerated to a flow rate of 200 m/sec by the nozzle. Atomized water was supplied at a rate of 21.2 kg/h from the water spray nozzle. At this time, the reduction reactor portion above the water nozzle had a temperature of 820°C, while the carbonation reactor portion above the nozzle had a temperature of 340°C.
- 20 Dust and particles were collected through the cyclone at a rate of 9.5 kg/h. When analyzed, the dust and particles were found to contain 92.4% of CaCO<sub>3</sub>, 3.5% of CaS, 2.7% of CaSO<sub>4</sub> and 1.4% of others. On the other hand, a gas stream having a temperature of 340°C and containing 2.4% of H<sub>2</sub>S was collected from an upper portion of the cyclone.

## 25 EXPERIMENT II

The procedure of EXPERIMENT I was repeated with the exception of the following.

- \*Solid containing calcium salt of sulfuric oxyacid:
- Used Ca-type absorbent (anhydrous gypsum content 43.7%)
- 30 \*Mean particle size: 2 microns
- \*Rate of supply of particles: 20 kg/h
- \*Flow rate of carrier gas: 25 Nm<sup>3</sup>/h
- \*Speed of carrier gas from dispersing nozzle: 300 m/sec
- \*Rate of supply of atomized water: 20.0 kg/h
- 35 \*Temperature of reduction reaction: 810°C
- \*Temperature of carbonation reaction: 335°C

- Consequently, dust and particles were collected from the cyclone at a rate of 21.1 kg/h. When analyzed, the dust and particles were found to contain 67.7% of CaCO<sub>3</sub>, 0.7% of CaS, 0.4% of CaSO<sub>4</sub> and 31.2% of others. On the other hand, a gas stream containing 1.5% of H<sub>2</sub>S and having a temperature of 335°C was collected from the upper portion of the cyclone.

- Fig. 2 shows an exhaust gas purifying system including the treatment circuit of Fig. 1. The system is an example as used for a thermoelectric power plant of 1000 MW class specifically designed for burning coal. With reference to the drawing, indicated at 13 is a coal burning boiler, in which coal is burned with air supplied by a blower 14 through an air heater 15 and which produces a combustion exhaust gas containing fly ash and harmful acid substances. Fine particles of a Ca-type absorbent, for example, finely divided limestone (CaCO<sub>3</sub>) having a mean particle size of 1 to 3 microns is sprayed into the top of the boiler 13 via a feed line 16. Consequently, the particulate absorbent is retained at a temperature of 900 to 1100°C for about 2 to about 3 seconds, whereby CaCO<sub>3</sub> is thermally decomposed instantaneously to give highly reactive CaO according to Equation (2). The CaO further undergoes the reactions of Equations (3) and (4), absorbing sulfur oxides and forming calcium sulfate (CaSO<sub>4</sub>) on the surface of the absorbent particles. The reactivity of the CaO is about 40 to about 50%, and unreacted CaO remains as it is in the interior of the particles. The heat evolved from the reactions is utilized by the boiler 13.

- The exhaust gas from the boiler 13 is passed through a denitrating unit 17, which removes nitrogen oxides from the gas. Via the air heater 15, the gas then enters a dust collecting unit 18, in which the used particulate absorbent and soot and dust containing fly ash are removed from the gas stream. The exhaust gas thus purified is then released to the atmosphere through a chimney 19. According to the invention, desulfurization is conducted at a high temperature of 900 to 1100°C, so that the exhaust gas has a reduced acid dew-point temperature. Consequently, the exhaust gas as released from the chimney 19 to the atmosphere has a temperature of about 100°C as reduced from the conventional temperature level of 140 to 150°C. This means that an increased amount of heat can be utilized by the boiler 13. Before reaching the dust collecting unit 18, the particulate absorbent absorbs hydrogen fluoride (HF) and hydrogen

chloride (HCl) from the exhaust gas, in addition to the sulfur oxides, but since the  $\text{CaF}_2$  and  $\text{CaCl}_2$  consequently formed do not participate in the subsequent treatment of the absorbent, these halides will not be described.

The soot, dust and particles collected by the unit 18 are led through a hopper 20 to an air classifier 21, by which they are separated into a coarse particle portion primarily containing fly ash of 12 to 15 microns in mean particle size, and a fine particle portion chiefly containing the used absorbent. The coarse particle portion separated off is stored in a container 22. The fine particle portion is led through a hopper 1 into a regenerating treatment circuit.

The regeneration circuit shown in Fig. 2, like the one shown in Fig. 1, includes an ejector 2, reduction reactor 3, reducing gas generator 4, carbonation reactor 5 having a cooler in the form of a heat exchanger, dust collecting unit 7, calcium carbonate hopper 8, hydrogen sulfide collector 9, feedback line 10 having a compressor 11, and purge line 12. The dust collecting unit 7 comprises a cyclone 23 and a bag filter 24 in combination. The hydrogen sulfide collector 9 comprises a cooler 25 having a cooling water circulation pump 26, a hydrogen sulfide absorption column 27 and a stripper 28. The stripper 28 is connected to a hydrogen sulfide container 29.

The  $\text{CaSO}_4$  component contained in the used absorbent fed to the reduction reactor 3 through the ejector 2 is reduced to  $\text{CaS}$  by the reactions of Equations (5) and (6) in the hot reducing gas from the generator 4. The  $\text{CaS}$  further reacts with carbon dioxide and water vapor in the carbonation reactor 5 according to Equation (7), forming  $\text{CaCO}_3$ . Consequently, the absorbent is regenerated, and  $\text{H}_2\text{S}$  is produced. During the carbonation reaction, the unreacted component ( $\text{CaO}$ ) inside the absorbent particles also undergoes the following reaction and is carbonated.



The reduction reaction and the carbonation reaction described above are each exothermic, and the heat of reaction is recovered by the heat exchanger 6.

The gas stream flowing out from the carbonation reactor 5 and containing the regenerated absorbent,  $\text{H}_2\text{S}$  and other unreacted gas components is subjected to solid-gas separation by the dust collecting unit 7. The particulate absorber separated off is fed back to the boiler 13 via the calcium carbonate hopper 8, rotary valve 30, ejector 31 and feed line 16. Since some of the absorbent particles are lost when classified by the air classifier 21, the feed line is replenished with a fresh absorber (which need not always contain  $\text{CaCO}_3$  but may contain  $\text{CaO}$  or  $\text{Ca(OH)}_2$ ) from an absorbent feeder 32 via a hopper 33, rotary valve 34 and ejector 35 to compensate for the loss. Indicated at 36 is a feeding compressor connected to the feed line 16.

The gas stream flowing out from the dust collecting unit 7 is cooled to about  $40^\circ\text{C}$  by the cooler 25 and then subjected to an amine washing step by the absorption column 27 and the stripper 28, whereby  $\text{H}_2\text{S}$  only is separated off for collection. The collected  $\text{H}_2\text{S}$  is stored in the container 29 and is treated, for example, by the Claus process at a suitable time. Indicated at 37 and 38 are elemental sulfur and water vapor resulting from the Claus process.

The gas stream flowing out from the hydrogen sulfide collector 9 is returned to the reduction reactor 10 by the compressor 11 via the feedback line 10. The gas stream is partly released to the outside via the purge line 12.

If it is attempted to reduce the amount of absorbent particles to be lost at the air classifier 21, the particulate material to be sent to the absorbent regeneration circuit downstream thereof will contain an increased amount of impurities (fly ash, etc.), giving an increased load to the regeneration circuit. Accordingly the ratio of separation to be conducted by the classifier 21 needs to be set in view of the balance between the amount of loss of absorbent and the load on the regeneration circuit.

The exhaust gas purifying system shown in Fig. 2 has the following advantages.

(a) Since used  $\text{Ca}$ -type absorbent is recycled for reuse upon regeneration, the exhaust gas can be purified efficiently with use of a smaller amount of absorbent without entailing the troublesome problem of by-products.

(b) Recycling of the absorbent which has been pulverized once serves to reduce the power for pulverization.

(c) The process from the desulfurization with the absorbent through the regeneration of the absorbent (the series of steps up to the dust collecting unit 7) is practiced continuously in a dry state and is therefore low in heat loss. Further the heat developed from the desulfurization and regeneration is effectively used by the boiler 13 and heat exchanger 6 to achieve an improved energy efficiency. The present method is free of the problem of effluent treatment which is encountered with the wet or semi-wet process and which could cause secondary pollution.

(d) The boiler 13 and dust collecting unit 15, which serve also as desulfurizing units, render the system compact.

(e) Because the desulfurization with the absorbent is conducted at a high temperature of  $900$  to  $1100^\circ\text{C}$ ,  $\text{SO}_3$  which is more harmful than  $\text{SO}_2$  and difficult to remove at lower temperatures



(SO<sub>3</sub> suspends in the exhaust gas in the form of stable minute crystals at low temperatures) can be removed effectively.

#### CLAIMS

- 5 1. A method of treating solids containing the calcium salt of a sulfuric oxyacid comprising feeding to a reduction reactor a reducing gas stream containing hydrogen and/or carbon monoxide and having a first predetermined temperature and dry particles containing the calcium salt of sulfuric oxyacid and having a predetermined mean particle size to reduce the calcium salt to calcium sulfide, subsequently cooling the gas stream obtained from the reduction reactor to a  
10 second temperature in a carbonation reactor to react the calcium sulfide with carbon dioxide and water vapor and produce calcium carbonate and hydrogen sulfide, guiding the resulting gas stream from the carbonation reactor into a dust collecting unit to collect solid particles, and further collecting the hydrogen sulfide from the gas stream flowing out from the dust collecting unit.
- 15 2. A method as defined in claim 1 wherein the calcium salt of sulfuric oxyacid comprises one or an optional combination of calcium sulfate, calcium sulfite, calcium thiosulfate and calcium polythionate.
3. A method as defined in claim 1 wherein the first temperature is 700 to 900°C.
4. A method as defined in claim 1 wherein the second temperature is 300 to 500°C.
- 20 5. A method as defined in claim 1 wherein the reducing gas stream is obtained by partially burning a hydrocarbon with water vapor and concentrated oxygen.
6. A method as defined in claim 1 wherein the gas separated from the collected hydrogen sulfide is fed back to the reduction reactor as a carrier gas for the dry particles.
7. A method of purifying an exhaust gas containing sulfur oxides by spraying dry particles of  
25 a Ca-type absorbent having a predetermined mean particle size into the exhaust gas to cause the absorbent to absorb the sulfur oxides and thereafter collecting by a dust collecting unit the absorbent particles along with other particles contained in the exhaust gas, the method being characterized by feeding to a reduction reactor the used absorbent particles collected by the dust collecting unit and a reducing gas stream containing hydrogen and/or carbon monoxide and  
30 having a first predetermined temperature to reduce calcium sulfate contained in the used absorbent particles to calcium sulfide, subsequently cooling the gas stream obtained from the reduction reactor to a second temperature in a carbonation reactor to react the calcium sulfide with carbon dioxide and water vapor and produce calcium carbonate and hydrogen sulfide, guiding the resulting gas stream from the carbonation reactor into a second dust collecting unit to collect  
35 solid particles, and spraying the solid particles again into the exhaust gas as regenerated absorbent particles.
8. A method as defined in claim 7 wherein the hydrogen sulfide is collected from the gas stream flowing out from the second dust collecting unit, and the remaining gas is thereafter fed back to the reduction reactor as a carrier gas.
- 40 9. A method as defined in claim 7 wherein the particles collected by the first dust collecting unit are classified into a coarse particle portion primarily containing fly ash and a fine particle portion primarily containing the used absorbent particles not larger than a predetermined particle size, and the fine particle portion only is fed to the reduction reactor.
10. A method as defined in claim 7 wherein the Ca-type absorbent comprises one or an  
45 optional combination of limestone, slaked lime, dolomite, slaked dolomite and calcined dolomite.
11. A method of treating solids containing the calcium salt of a sulfuric oxyacid substantially as described herein with reference to the accompanying drawings and/or to any one or more of the examples.
12. A method of purifying an exhaust gas containing sulfur oxides, substantially as described  
50 herein with references to the accompanying drawings and/or to any one or more of the examples.

